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Combining Low-Pressure CO_2 Capture and Hydrogenation To Form Methanol

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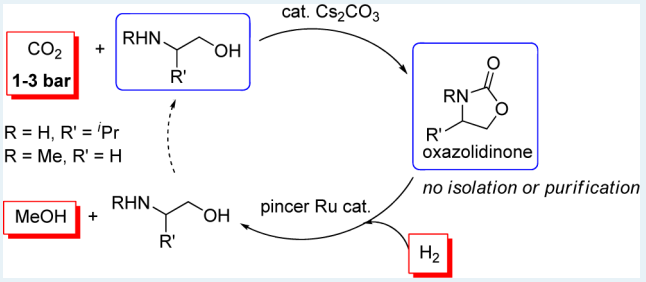
Supporting Information

ABSTRACT: This paper describes a novel approach to CO_2 hydrogenation, in which CO_2 capture with aminoethanols at low pressure is coupled with hydrogenation of the captured product, oxazolidinone, directly to MeOH. In particular, (2-methylamino)ethanol or valinol captures CO_2 at 1−3 bar in the presence of catalytic Cs_2CO_3 to give the corresponding oxazolidinones in up to 65−70 and 90−95% yields, respectively. Efficient hydrogenation of oxazolidinones was achieved using PNN pincer Ru catalysts to give the corresponding aminoethanol (up to 95−100% yield) and MeOH (up to 78−92% yield). We also have shown that both CO_2 capture and oxazolidinone hydrogenation can be performed in the same reaction mixture using a simple protocol that avoids intermediate isolation or purification steps. For example, CO_2 can be captured by valinol at 1 bar with Cs_2CO_3 catalyst followed by 4-isopropyl-2-oxazolidinone hydrogenation in the presence of a bipy-based pincer Ru catalyst to produce MeOH in 50% yield after two steps.



KEYWORDS: *carbon dioxide, hydrogenation, methanol, oxazolidinone, ethanolamine, ruthenium, pincer*

INTRODUCTION

Capturing and converting CO_2 gas to a liquid fuel is an important challenge for the future of a sustainable economy. In particular, the reaction of CO_2 with H_2, the latter obtained via renewable energy methods such as solar-driven water splitting, to form a liquid methanol fuel is an important pathway outlined in "The Methanol Economy".[1] Because the integration of new energy sources into developed economies must necessarily proceed in a sequential manner, recent interest has focused on utilizing CO_2 streams from readily available power plant discharge or from natural gas streams, with a view toward transforming this waste gas to methanol fuel by reacting it with hydrogen in an energy-efficient manner.[2] Many efforts of power utilities today are devoted to CO_2 capture and storage, meaning a recycling option via converting waste CO_2 to methanol fuel is particularly attractive.

Various technologies have been developed for the minimization of CO_2 emissions to the atmosphere from the flue gas streams of fossil-fuel-powered plants. Most common methods are based on chemical CO_2 absorption using amines or aminoalcohols as solvents, with monoethanolamine (MEA, **1**) being the most common CO_2 capture agent (Scheme 1).[3] Current developed technologies for CO_2 capture involve several steps, including CO_2 absorption to produce hydrocarbonate (eq 1, Scheme 1) and carbamate (eq 2, Scheme 1) salts,[4,5] followed by subsequent release of CO_2 by the high-temperature decomposition of these salts.[6,7] The CO_2 gas separated by such methods is then compressed and transported to a storage site, while amine solutions are partially recycled.[6,8]

Scheme 1. Chemical Processes That Occur during CO_2 Capture with Amines

RNH_2 = H_2N–OH

1 = MEA

$CO_2 + H_2O + RNH_2 \rightleftharpoons HCO_3^- + RNH_3^+$ (1)

$CO_2 + 2RNH_2 \rightleftharpoons RNHCOO^- + RNH_3^+$ (2)

One of the major problems of such processes is thermal degradation of amines occurring during thermal treatment of the hydrocarbonate and carbamate salts to liberate CO_2 and is responsible for the large amount of amine waste resulting from such CO_2 capture operations. In 2009, for example, Bellona Foundation reported that "a typical CO_2 capture plant with the capacity of 1 million tonnes of CO_2 annually is expected to produce from 300 to 3000 tonnes of amine waste annually", thereby reducing the economic viability of such processes.[9] The most common reported thermal degradation product from CO_2 capture with monoethanolamine is 2-oxazolidinone (**2** in Scheme 2), which further reacts to give other products of decomposition (**3**, **4**, and **5** in Scheme 2).[10] An additional energy penalty comes from the need to heat the carbonate salt solutions to high temperatures in order to release CO_2 and regenerate the amine and also from the subsequent CO_2

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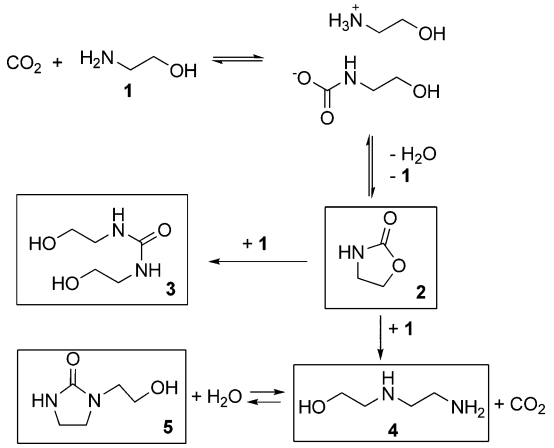
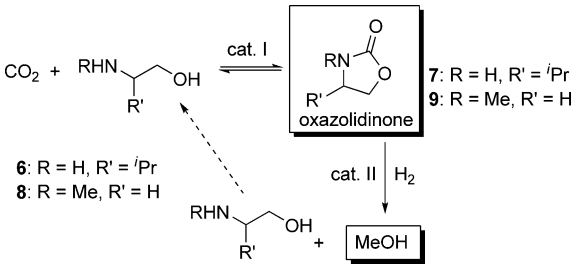
Scheme 2. Byproducts of CO_2 Capture with Monoethanolamine 1 [2 = 2-Oxazolidinone, 3 = *N,N′*-(2-Hydroxyethyl)urea, 4 = *N*-(2-Hydroxyethyl)ethylenediamine (HEEDA); 5 = 1-(2-Hydroxyethyl)-2-imidazolidone (HEIA)]



sequestration.[8] Therefore, it would be highly beneficial if, instead of releasing and storing the CO_2 gas, the products of CO_2 chemical absorption with amines were to be directly converted into a liquid fuel such as methanol.

Taking a page from industry, where aminoalcohols are used to fix CO_2 streams and thus "capture" the gas, we hereby report a procedure where we capture CO_2 at low pressure and use the in situ created capture product, an oxazolidinone compound, to generate methanol in one step in yields up to a total of ~50% (Scheme 3). These results represent a novel approach for the

Scheme 3. Proposed Scheme for Selective CO_2 Capture and Conversion to MeOH

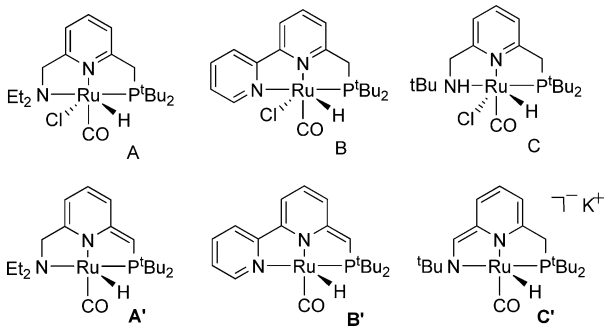


use of CO_2 capture products directly for their conversion to MeOH, thus avoiding additional energy costs required for CO_2 thermal regeneration and storage. This approach may be of practical use to the power utility industry which uses a similar chemical process to capture CO_2 waste gas.[9]

In the proposed approach, the selective formation of oxazolidinone via CO_2 capture at low pressures is accomplished through the use of Cs_2CO_3 as a catalyst, while hydrogenation of the latter to produce MeOH and regenerated aminoalcohol is achieved in the same reaction mixture using Ru pincer catalysts developed in our group (Scheme 3 and Chart 1).

This approach is conceptually different from the currently known examples for direct hydrogenation of CO_2 to MeOH using transition metal catalysts.[11] In particular, the existing homogeneous catalytic systems for direct CO_2 hydrogenation to MeOH rely on the use of pressurized CO_2 gas (10–20 bar), thus adding the cost of CO_2 concentration and pressurization,

Chart 1. Ru Hydrogenation Catalysts Used in This Study



making such processes less attractive.[12−15] By contrast, the approach presented here allows for CO_2 capture at low pressure and direct utilization of the formed captured species for the generation of a valuable product: MeOH. It appears that, while this article was under preparation, a similar approach was recently reported by Sanford et al. based on the use of dimethylamine for hydrogenation of CO_2 to formamide and MeOH.[16] For comparison, the previously reported system for CO_2 capture in an amidine base/alcohol mixture failed to produce MeOH upon catalytic hydrogenation, and only formate ester and formate salt were formed.[17]

RESULTS AND DISCUSSION

CO_2 Capture. CO_2 capture using monoethanolamine and other aminoalcohols has been studied previously and proceeds through the formation of hydrocarbonate salts as well as carbamate salts with a protonated amine as the counterion. During thermal decomposition of these salts that takes place during the CO_2 liberation step in CO_2 capture plants, oxazolidinone **2** (Scheme 2) is formed as a byproduct which further reacts to give **3**, **4**, and **5** (Scheme 2). However, the formation of oxazolidinone can be made selective through the use of catalysts such as $^nBu_2SnO$,[18] CeO_2,[19,20] or other systems. Considering that CO_2 capture from gas streams should occur at low partial CO_2 pressures, we focused our attention on a recently reported method for selective oxazolidinone formation from aminoalcohols and 1 atm of CO_2 using a Cs_2CO_3 catalyst in dimethylsulfoxide (DMSO) solvent developed by Saito.[21] According to Saito's density functional theory results, monoethanolamine (**1**) was not an ideal substrate for such cyclization due to unfavorable thermodynamics of the reaction, which leads to low yields when only 1 atm of CO_2 is used. However, substrates with bulky substituents in the α-position to the amine group, such as valinol **6** (derived from the natural amino acid, valine), show a higher propensity toward cyclization and form the corresponding oxazolidinone product in up to 90% yield at a pressure of 1 atm of CO_2.[21]

Indeed, when monoethanolamine **1** was reacted under 2 bar of CO_2 in the presence of 10 mol % of Cs_2CO_3 in DMSO for 90 h at 150 °C, only 19% of 2-oxazolidinone **2** was obtained (Scheme 4a). By contrast, valinol **6** reacted much more readily to produce the corresponding 4-isopropyl-2-oxazolidinone **7** in 90–95% yield after heating at 150 °C for 24 h under 1 bar of CO_2 (Scheme 4b). A control experiment using 1 mmol of Cs_2CO_3 and 1 mmol of valinol in the absence of CO_2 gas does not generate the oxazolidinone product, showing that Cs_2CO_3 does not act as a source of CO_2 in this reaction.

We have also examined the reactivity of 2-(methylamino)-ethanol **8** under these conditions. **8** was proposed previously as

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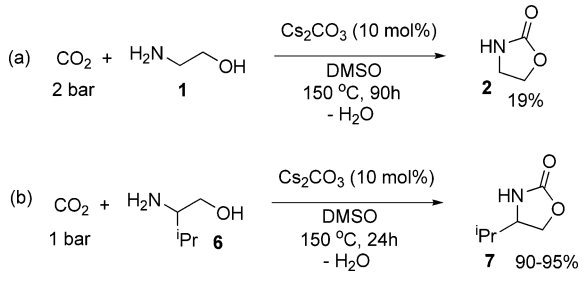
Scheme 4. CO_2 Capture with Monoethanolamine (a) and Valinol (b)



an alternative for monoethanolamine in CO_2 capture processes, and it has a lower commercial price compared to valinol.[22] When 2-(methylamino)ethanol was heated under 3 bar of CO_2 in DMSO in the presence of 15 mol % of Cs_2CO_3 for 72 h at 150 °C, the corresponding 3-methyl-2-oxazolidinone product **9** was obtained in ~64−66% crude yield (Table 1, entry 3). The other products of the reaction are most likely bicarbonate and carbamic acid salts of the protonated 2-(methylamino)ethanol, which were previously reported as byproducts of CO_2 capture with 2-(methylamino)ethanol.[22] Attempted replacement of Cs_2CO_3 with less expensive K_2CO_3 failed to produce satisfactory results (compare entries 1 and 4). The reaction catalyzed by Cs_2CO_3 in less polar solvents, such as THF or dioxane, also led to low yields of the product, likely due to the low solubility of Cs_2CO_3 in these solvents (compare entries 1, 5, and 6).

The CO_2 capture with 2-(methylamino)ethanol is also catalyzed by $^nBu_2SnO$ in toluene; however, this catalytic system typically required higher temperature to obtain comparable yields of 3-methyl-2-oxazolidinone (entry 7). In addition, $^nBu_2SnO$ is not compatible with the Ru pincer catalyst that is used for hydrogenation of oxazolidinone products to MeOH (see next sections).

These results indicate that using a simple catalyst, Cs_2CO_3, selective CO_2 capture at 1−3 bar of CO_2 can be achieved with valinol and 2-(methylamino)ethanol in DMSO to give oxazolidinones as the major products.

Hydrogenation of Oxazolidinones: Catalyst and Reaction Condition Screening. Hydrogenation of noncyclic carbamic esters using a Ru pincer catalyst has been previously reported by our group; however, cyclic substrates were not examined in this study.[23] We are unaware of literature reports of hydrogenation of oxazolidinones. In the search for a system for oxazolidinone hydrogenation to MeOH, we first examined the reactivity of various Ru catalysts in hydrogenation of 3-methyl-2-oxazolidinone as a model substrate (Table 2). This model reaction was performed in THF as a solvent using pincer Ru catalysts developed in our group (**A**, **B**, and **C**). Catalyst **A** is currently commercially available. An additive of 1 equiv of base, ^{t}BuOK, was required in order to activate the catalyst precursors **A** and **B** and form a dearomatized catalytically active species **A′** and **B′**, respectively, in situ (Chart 1).[24,25] Two equivalents of ^{t}BuOK was used to activate complex **C** for the in situ generation of **C′**, as shown in previous studies (Chart 1).[26]

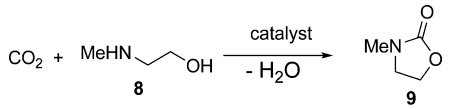
Comparison of catalysts **A**, **B**, and **C** at 0.5 mol % catalyst loading shows that catalyst **B** gives the highest yields of MeOH and 2-(methylamino)ethanol **8** under these conditions (Table 2, entries 1−3), 70 and 80%, respectively. Better yields of MeOH and **8** can be obtained at similar times using 1 mol % catalyst loading (Table 2, entries 4 and 5). Using a THF/water (2:1) solution leads to very low conversions (Table 2, entries 6 and 7).

Finally, hydrogenation of 3-methyl-2-oxazolidinone was examined in DMSO as a solvent, as the Cs_2CO_3/DMSO system was shown to be optimal for CO_2 capture to selectively form oxazolidinones. While DMSO was not the ideal solvent for hydrogenation of 3-methyl-2-oxazolidinone at 1 mol % catalyst loading (Table 2, entry 8), increasing the catalyst loading to 2 mol % and prolonging reaction time led to efficient conversion of 3-methyl-2-oxazolidinone to 2-(methylamino)-ethanol and MeOH in 96 and 78% yields, respectively (Table 2, entry 9). Under these conditions, less than 2% of Me_2S was formed through DMSO hydrogenation, suggesting that the catalyst was selective toward hydrogenation of the oxazolidinone substrate in the presence of DMSO.

Similarly, hydrogenation of 4-isopropyl-2-oxazolidinone in DMSO in the presence of 2 mol % of **B** and 2 mol % of ^{t}BuOK led to the selective formation of valinol (>99%) and MeOH (83% yield) in DMSO as a solvent (Scheme 5a). For comparison, hydrogenation of **7** in DMSO under similar conditions in the presence of the commercially available Ru catalyst, RuMACHO (2 mol %) and ^{t}BuOK (2 mol %), leads to an unselective reaction and the formation of only 10% of MeOH at 41% conversion of **7** (see Supporting Information for more detail).

Overall, these results demonstrate that catalyst **B** is the most efficient catalyst for oxazolidinone hydrogenation to form

Table 1. CO_2 Capture with 2-(Methylamino)ethanol[a]



entry	catalyst (mol %)	solvent	CO_2 pressure (bar)	T (°C)	t (h)	conversion (%)	yield[b] of **9** (%)
1	Cs_2CO_3 (10)	DMSO	1	150	48	95	50
2	Cs_2CO_3 (15)	DMSO	3	160	48	99	70
3	Cs_2CO_3 (15)	DMSO	3	150	53	99	66
4	K_2CO_3 (10)	DMSO	1	150	48	95	<30
5	Cs_2CO_3 (10)	THF	1	150	48	<10	nd[c]
6	Cs_2CO_3 (10)	dioxane	1	150	48	<10	nd[c]
7	$^nBu_2SnO$ (10)	toluene	1	160	54	98	64

[a]Typical reaction conditions: substrate **8** (1 mmol), catalyst, and solvent were heated in a Fischer−Porter tube under 1−8 bar of CO_2 pressure. [b]Yields were determined by NMR using pyridine or DMSO as an internal standard. [c]Not detected.

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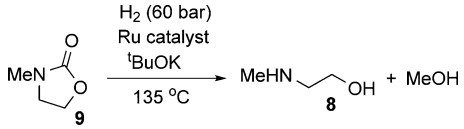
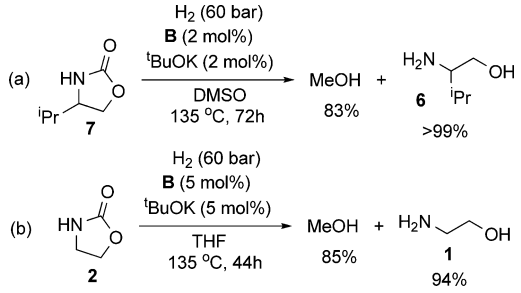
Table 2. Ru-Catalyzed Hydrogenation of 3-Methyl-2-oxazolidinone[a]



entry	catalyst (mol %)	solvent	t (h)	conversion (%)	yield[b] of **8** (%)	yield[b] of MeOH (%)
1	**A** (0.5) ^{t}BuOK (0.5)	THF	23	57	57	51
2	**B** (0.5) ^{t}BuOK (0.5)	THF	19	80	80	70
3	**C** (0.5) ^{t}BuOK (1)	THF	19	64	64	56
4	**A** (1) ^{t}BuOK (1)	THF	19	>99	95	84
5	**B** (1) ^{t}BuOK (1)	THF	19	>99	100	92
6	**A** (1) ^{t}BuOK (1)	THF/H_2O[c]	19	8	7	7
7	**B** (1) ^{t}BuOK (1)	THF/H_2O[c]	21	4	<1	<1
8	**B** (1) ^{t}BuOK (1)	DMSO	21	64	36	32
9	**B** (2) ^{t}BuOK (2)	DMSO	48	>92	96	78

[a]Typical reaction conditions: substrate **9**, 0.5−2 mol % of Ru catalyst, and 0.5−2 mol % of ^{t}BuOK were heated at 135 °C under 60 bar of H_2 in a stainless steel autoclave; the reaction mixtures were analyzed by NMR and GC-MS. [b]Yields were determined by NMR integration versus internal standard. [c]2:1 v/v THF/H_2O ratio.

Scheme 5. Hydrogenation of 4-Isopropyl-2-oxazolidinone (a) and 2-Oxazolidinone (b) Catalyzed by B



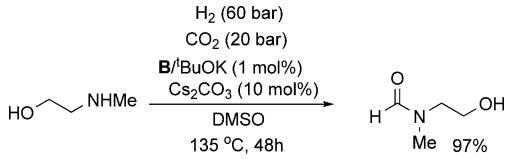
selectively the corresponding aminoalcohol and methanol in high yields. This catalytic reactivity is general and is applied to other substrates, as well, including hydrogenation of an unsubstituted 2-oxazolidinone, although the latter required higher catalyst loading (5 mol %) to achieve good yields and conversions (Scheme 5b).

The high yields of MeOH obtained by hydrogenation of 3-methyl-2-oxazolidinone and 4-isopropyl-2-oxazolidinone in DMSO as a solvent imply that **B** can be a suitable catalyst for developing a combined process for CO_2 capture at low pressure coupled with hydrogenation to MeOH, as shown below.

Combining CO_2 Capture and Hydrogenation To Form MeOH. Based on the results above, we decided to explore a combined one-step process for CO_2 hydrogenation to MeOH at low CO_2 pressure, without isolation of the intermediate.

First, we attempted direct CO_2 hydrogenation in the presence of 2-(methylamino)ethanol **8** under pressurized CO_2 (20 bar) and H_2 (60 bar) in the presence of Cs_2CO_3 (10 mol %), **B** (1 mol %), and ^{t}BuOK (1 mol %) in DMSO or THF as a solvent. However, under these conditions, no MeOH was formed, and the major product, formed in 97% yield, was identified as *N*-(2-hydroxyethyl)-*N*-methylformamide (OHC)-N(Me)(CH_2CH_2OH) by ESI and GC-MS (Scheme 6). The

Scheme 6. Attempted Direct Hydrogenation of CO_2 in the Presence of 2-(Methylamino)ethanol, Catalyst B, and Cs_2CO_3



formation of the formamide was also observed in the absence of Cs_2CO_3 and likely results from Ru-catalyzed CO_2 hydrogenation in the presence of a secondary amine.[27] Similarly, screening of other reaction conditions for hydrogenation of CO_2 directly in the presence of 2-(methylamino)ethanol **8** or valinol **6** in a solution containing **B**/^{t}BuOK and Cs_2CO_3 (or ^{n}Bu_2SnO) failed to produce MeOH (see Supporting Information for more detail).

These results suggest that catalyst **B** cannot effectively hydrogenate formamides (or carbamates) in the presence of CO_2 gas. Complex **B** could also be modified or deactivated via the reactivity with CO_2 studied previously by our group and by Sanford.[28,29]

We then proposed that the CO_2 capture and Ru-catalyzed hydrogenation steps should be performed consecutively to avoid exposure of catalyst **B** to CO_2 gas. However, since both CO_2 capture and oxazolidinone hydrogenation can be performed in DMSO, both steps can be carried out in the

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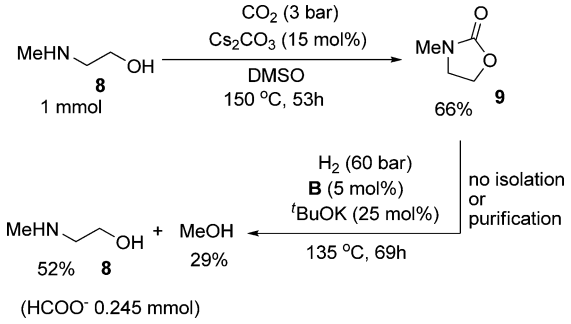
same solution, without isolation of oxazolidinone. This would provide a simple protocol for captured CO_2 hydrogenation to MeOH that avoids the intermediate isolation or purification steps.

This modified protocol was first examined using 2-(methylamino)ethanol **8** as a CO_2 capture agent (Scheme 7).

Scheme 7. CO_2 Capture/Hydrogenation to MeOH Using 2-(Methylamino)ethanol



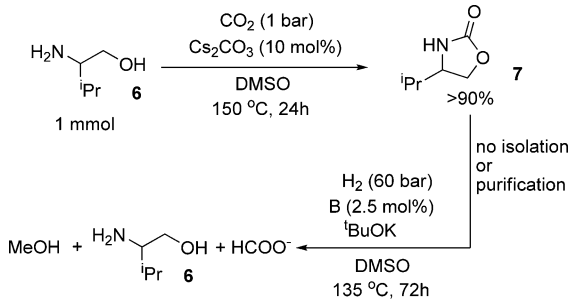
First, the CO_2 capture step was performed as described above, using 15 mol % of Cs_2CO_3 in DMSO and 3 bar of CO_2. After being heated for 72 h at 150 °C, the resulting solution containing 66% of 3-methyl-2-oxazolidinone **9** was evacuated at room temperature to remove excess CO_2 gas and was then combined with catalyst **B** (5 mol %) and ^{t}BuOK (25 mol %). Subsequent hydrogenation under 60 bar of H_2 at 135 °C produced MeOH and 2-(methylamino)ethanol **8** in 29 and 52% yields, respectively, after 69 h. Formate salt was also present as a major byproduct (24% yield based on **8**) that likely results from a Ru-catalyzed hydrogenation of remaining CO_2 or hydrocarbonate salts.[30−33]

A large excess of ^{t}BuOK (25 mol %) relative to the catalyst is required in this reaction to obtain significant conversion to MeOH. For comparison, when 1 equiv of ^{t}BuOK was used, only a trace amount of MeOH was formed, while starting materials remained mostly unreacted. Excess base is most likely needed to neutralize acidic byproducts of CO_2 capture (e.g., hydrocarbonate and formate salts of a protonated 2-(methylamino)ethanol), which may react with a dearomatized catalyst **B′**, leading to its deactivation.

An analogous protocol using a lower catalyst loading, 2.5 mol % of **B** and 20 mol % of ^{t}BuOK, produced MeOH and 2-(methylamino)ethanol in 21 and 38% yields, respectively, after 48 h. A control experiment showed that when Cs_2CO_3 alone was heated in DMSO under 60 bar of H_2 in the presence of **B** (10 mol %) and ^{t}BuOK (10 mol %), no methanol formation was observed, indicating that Cs_2CO_3 does not act as a source of MeOH. Thus, these initial results demonstrate that MeOH can be obtained in a total yield of 29% in a simple reaction sequence and in the same solution, without intermediate product isolation or purification steps.

To further improve this process, this protocol was then tested using valinol **6**, which was shown to capture CO_2 more selectively under only 1 bar of CO_2. First, CO_2 capture was performed as described above, using 10 mol % of Cs_2CO_3 under 1 bar of CO_2 in DMSO to produce 4-isopropyl-2-oxazolidinone **7** in >90% yield after heating for 24 h at 150 °C (see above). After removal of CO_2 under vacuum and addition of **B** (2.5 mol %) and ^{t}BuOK (25 mol %), hydrogenation under 60 bar of H_2 produced MeOH and valinol in 37 and 62% yields, respectively, after heating at 135 °C for 72 h (Table 3, entry 1). However, when less amounts of ^{t}BuOK were used (entries 2 and 3), the yield of MeOH decreased.

Table 3. CO_2 Capture/Hydrogenation to MeOH Using Valinol[a]



entry	catalyst (mol %)	yield[b] of **7** (%)	yield[b] of MeOH (%)	yield[b] of **6** (%)	$HCOO^-$ (mmol)[b]
1	**B** (2.5) ^{t}BuOK (25)	9	37	62	0.193
2	**B** (2.5) ^{t}BuOK (15)	39	21	34	0.260
3	**B** (2.5) ^{t}BuOK (6)	67	6	~12	0.141
4[c]	**B** (2.5) ^{t}BuOK (25)	nd[e]	53	74	0.057
5[d]	**B** (2.5) ^{t}BuOK (25)	36	45	63	nd[e]
6[c]	**B** (2.5) ^{t}BuOK (10)	6	44	63	0.089

[a]Typical reaction conditions: 1 mmol of valinol and 0.1 mmol of Cs_2CO_3 in DMSO were heated at 150 °C for 24 h; the reaction mixture was then degassed under vacuum at room temperature for 20 min; **B** and ^{t}BuOK were added, and the reaction mixture was heated under H_2 (60 bar) at 135 °C for 72 h. [b]Yields after the hydrogenation step. [c]Reaction mixture was filtered before hydrogenation. [d]Reaction mixture was diluted with toluene and filtered before hydrogenation. [e]Not detected.

Because formate salt was still present among the reaction products, this could indicate that inorganic impurities such as cesium or potassium hydrocarbonate salts could still be present in the reaction mixture and undergo further hydrogenation in the presence of a Ru catalyst upon heating.[30−33] To remove possible inorganic contaminants, the reaction mixture after CO_2 capture step was combined with **B** (2.5 mol %) and ^{t}BuOK (25 mol %) and then filtered through a Celite plug at room temperature, and the resulting clear solution was subjected to typical hydrogenation conditions (60 bar of H_2, 135 °C, 72 h). This led to improved yields of MeOH and valinol, which were obtained in 53 and 74% yields, respectively (Table 3, entry 4). Accordingly, the fraction of formate salts significantly decreased. Attempted precipitation of inorganic salts with an equal volume of toluene from DMSO solution followed by filtration did not improve the results, and MeOH and valinol were obtained in 45 and 63% yields, respectively, under analogous conditions (entry 5).

This improved protocol also allowed us to lower the amount of ^{t}BuOK to 10 mol % to obtain MeOH and valinol in comparable yields, 44 and 63%, respectively, under analogous conditions (entry 6).

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Overall, these results demonstrate that selective CO_2 capture under mild conditions (1 bar of CO_2) can be combined with Ru-catalyzed hydrogenation of in situ formed oxazolidinone product to MeOH and aminoalcohol in a simple procedure that does not require isolation or purification of the captured oxazolidinone product. Although the yields in such a combined procedure are moderate, our study of the catalytic activity of complex **B** in hydrogenation of oxazolidinones (see above) shows that these results can potentially be improved by developing a process engineering solution and improving the catalyst activity. Presently, complex **B** is the only reported catalyst for the highly selective hydrogenation of oxazolidinones to generate MeOH and the corresponding aminoalcohol.

CONCLUSION

In summary, we have demonstrated a novel approach to CO_2 hydrogenation to MeOH in which CO_2 capture at low pressure with aminoalcohols is coupled with hydrogenation of the captured product, oxazolidinone, to form MeOH. This approach was inspired by the CO_2 capture industry which utilizes aminoalcohols to capture CO_2 from waste streams. However, the capture of oxazolidinone product has previously not been considered a useful precursor for the production of liquid fuel such as MeOH due to the lack of methods for such conversion. We have shown here that the Ru pincer complexes (**A**, **B**, and **C**) are active catalysts for the unprecedented hydrogenation of oxazolidinones, which are often formed as byproducts of CO_2 capture. Moreover, we have shown that both steps, CO_2 capture to selectively produce oxazolidinones and their subsequent hydrogenation to MeOH, can be performed in the same reaction mixture using a simple protocol that avoids intermediate isolation or purification steps. For example, using valinol for selective CO_2 capture at 1 bar catalyzed by Cs_2CO_3 and hydrogenation of corresponding oxazolidinone using catalyst **B** allowed us to obtain MeOH in up to ~50% total yield.

The advantage of this approach is that it allows one to utilize the CO_2 capture product directly for MeOH production, thus avoiding the energy costs associated with CO_2 regeneration from capture products and pressurization. This is conceptually different from other previously reported catalytic processes where pressurized CO_2 is used to produce MeOH. We hope that these conceptually new results will stimulate the development of novel processes for direct utilization of CO_2 capture products to produce liquid fuels or other value-added products.

EXPERIMENTAL SECTION

Typical Procedure for CO_2 Capture. A Fischer−Porter pressure tube equipped with a magnetic stirring bar was charged with Cs_2CO_3 (0.1−0.15 mmol), valinol, or 2-(methylamino)ethanol (1 mmol) and a preweighed amount of DMSO (1 mL). The Fischer−Porter tube was filled with CO_2 gas to 1 bar (for valinol) or 3 bar (for 2-(methylamino)-ethanol) pressure and heated at 150 °C for 24−72 h. The solution was cooled, and CO_2 was released. A sample of the reaction mixture was dissolved in D_2O or $CDCl_3$ and analyzed by NMR. Yields were determined versus DMSO as an internal standard.

Typical Procedure for Hydrogenation of Oxazolidinones. In a nitrogen-filled glovebox, an oven-dried 45 mL autoclave with a Teflon insert equipped with a magnetic stirring bar was charged with the Ru complex (10 μmol), ^{t}BuOK (10−20 μmol), oxazolidinone substrate (1 or 2 mmol), and 1.5 mL of the solvent. The autoclave was filled with H_2 gas (60 bar) and heated at 135 °C for an indicated period of time. The reaction mixture was then cooled before releasing H_2 pressure, then 10 or 20 μL of pyridine was added as a standard, and a sample of the reaction mixture (50−100 μL) was dissolved in 0.6 mL of D_2O or $CDCl_3$ and analyzed by ^{1}H NMR and GC-MS. Yields were determined by NMR integration versus pyridine as an internal standard.

The unaccounted mass balance for MeOH formation (for example, Table 2, entry 9) could be due to partial loss of a volatile MeOH product in the headspace.

Typical Procedure for Combined CO_2 Capture/Hydrogenation. A Fischer−Porter tube equipped with a magnetic stirring bar was charged with Cs_2CO_3, valinol, or 2-(methylamino)alcohol substrate (1 mmol) and 1 mL of DMSO and then filled with CO_2 at 1 bar (for reaction with valinol) or 3 bar (for reaction with 2-(methylaminoethanol). The reaction mixture was heated at 150 °C for 24 h (for reaction with valinol) or 53 h (for reaction with 2-(methylamino)ethanol). The solution was then cooled and stirred under vacuum for 20 min at room temperature to remove CO_2. A solution of complex **B** (25−50 μmol) and ^{t}BuOK (60−250 μmol) in 2 mL of DMSO was then added. The reaction mixture was then transferred to a 45 mL autoclave equipped with a magnetic stirring bar, filled with H_2 (60 bar), and heated at 135 °C for 72 h. After being cooled, H_2 was released and 20 μL of pyridine was added as a standard. A sample of the reaction mixture (50−100 μL) was dissolved in 0.6 mL of D_2O (or $CDCl_3$ in entry 5, Table 3) and analyzed by ^{1}H NMR. The yields were determined versus pyridine as an internal standard. In an optimized procedure (entries 4−6, Table 3), the reaction mixture after addition of **B** and ^{t}BuOK was filtered through a short Celite plug before being transferred to an autoclave.

ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00194.

General information, experimental details, and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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